Theoretical Equation of State for Highly Anharmonic Solids

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The possibility of quantitative theoretical prediction of absolute free energy, entropy and other thermodynamic properties of classical highly anharmonic solids is demonstrated. The equation of state proposed is based on the statistical theory of simple anharmonic crystals developed earlier [1] which accounts for correlations in displacements of atoms from their lattice sites. In this work the general expression for contribution of triple correlations is developed and numerical procedures for its evaluation proposed. The anharmonic, pair and triple correlation contributions to thermodynamic properties of Lennard-Jones FCC solid are computed accurately and their relative importance analyzed. Helmholtz free energy, entropy, internal energy and compressibility factor of Lennard-Jones solid were calculated in a wide range of temperatures and compared with the most accurate Monte Carlo data [2,3] available in the literature. The comparison reveals that our theoretical predictions are in an excellent agreement with simulation data in a whole range of temperatures and densities, including sublimation and melting lines. The analytical expression of Helmholtz free energy as a function of temperature and density suitable for calculation of all other thermodynamic properties of Lennard-Jones solid is presented.

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